

On Vapour-pressure and Osmotic Pressure of Strong Solutions.

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1. The relations between vapour-pressure, osmotic pressure, and concentration of solutions are of great interest, and have been the subject of recent communications by Lord Berkeley and Hartley, by Spens, and by Porter. I propose in the present paper to develop a theory of solutions, based on a simple relation between the vapour-pressure and the concentration, which appears to give a very fair account of the phenomena observed in the case of strong solutions, and is at the same time a natural extension of the present theory as applied to dilute solutions. Before discussing the theory itself, I propose to give fresh proofs of some of the more important relations already accepted, for the sake of indicating clearly the order of approximation attempted, and of illustrating methods of proof which I have employed in teaching for many years, but which do not appear to be generally known.

Relation between Vapour-pressure and Hydrostatic Pressure.

2. By considering the isothermal equilibrium of a liquid and its vapour in a capillary tube of radius r , Lord Kelvin* deduced the well-known relation between the vapour-pressure p at the curved surface and the normal vapour-pressure p_0 at a plane surface, in terms of the surface tension T , and the densities of the liquid and vapour ρ and σ ,

$$p - p_0 = 2T\sigma/r(\rho - \sigma), \quad (1)$$

where r is positive if the surface is convex. The effect was regarded by Lord Kelvin as being due to curvature, but Poynting† showed that it might be regarded simply as an effect of hydrostatic pressure, and explained the equilibrium of ice and water under pressure on this basis. Since the pressure P inside a spherical drop of radius r exceeds the vapour-pressure p outside it by $2T/r$, substituting $(P - p)$ for $2T/r$ we obtain,

$$p - p_0 = (P - p)\sigma/(\rho - \sigma) = (P - p_0)\sigma/\rho, \quad (2)$$

which is equivalent to the expression given by Poynting. Since the relation

* 'Phil. Mag.,' [4], vol. 42, p. 448, 1871.

† 'Phil. Mag.,' [12], p. 40, 1881.

applies only to small differences of pressure in this form, it is more convenient to write it in the differential notation

$$v \, dp = V \, dP, \quad (3)$$

which is perfectly general and accurate if V and v are the specific volumes of the liquid and vapour at the pressures P and p respectively. By integrating equation (3) between corresponding limits of P and p , the variation of vapour-pressure with pressure may be obtained with considerable accuracy over wide ranges of pressure and temperature. The principal source of uncertainty is the compressibility of the liquid. If we put $V = V_0(1 - \alpha P)$, assuming the compressibility α to be constant, and if we take $v = R'\theta/p - c + b^*$ (where $c - b$ represents the defect of volume of the vapour from the ideal volume $R\theta/p$, and is to a first approximation a function of the temperature only), we obtain

$$R'\theta \log_e (p/p_0) = (c - b)(p - p_0) + V_0(P - P_0) - \frac{1}{2}\alpha V_0(P^2 - P_0^2), \quad (4)$$

where P , p , and P_0 , p_0 , are corresponding limits of P and p . According to this equation it would require a pressure of about 2000 atmospheres only to increase the vapour-pressure of water fourfold at 27°C . The approximate equation (2), which is often applied to such calculations, would give upwards of 4600 atmospheres. The term $(c - b)(p - p_0)$ is negligible at this temperature, as p is so small, but it amounts to about 17 per cent. at 200°C ., if $p/p_0 = 4$. It has the effect of considerably reducing the pressure required when p is large.

Vapour-sieve Method.

3. It is easier to form a mental picture of the variation of vapour-pressure with hydrostatic pressure, if we imagine the liquid contained in a long vertical tube perforated with very fine holes. If the holes are fine enough and are not wetted by the liquid, the liquid cannot escape, but the vapour has free passage. If such a tube is surrounded by vapour in an isothermal enclosure, the liquid must be in equilibrium with its vapour at all points, which leads immediately to equation (3). If the holes are wetted by the liquid the same arrangement will apply for negative values of P . Poynting† deduces that the pressure of the vapour molecules in the interior of the liquid at any point of such a tube must be everywhere *proportional* to the pressure of the vapour immediately outside the tube. There is reason for believing that the vapour-pressure in the liquid is not merely proportional to that outside, but is *equal* to it, in other words that it is everywhere the same as if the liquid were

* Callendar, 'Roy. Soc. Proc.,' vol. 67, p. 270, 1900. R' is the gas-constant, $R = 1.98$ calories, divided by the molecular weight m of the vapour.

† *Loc. cit.*

absent. I have shown* that such an assumption appears to account satisfactorily for the variation of the specific heat in the case of water.

The same reasoning precisely applies if the vapour-sieve tube contains any solution in place of a pure liquid. Equilibrium will be rapidly established by condensation or evaporation of the vapour until condition (3) is satisfied. A column of pure solvent in equilibrium with the same vapour column must be in equilibrium with the solution at corresponding heights. If the holes in the vapour-sieve are fine enough to permit passage only to the vapour molecules, we may imagine the solution column surrounded by the solvent column without disturbing the equilibrium. The difference of hydrostatic pressure between the columns of solution and solvent at any height is the osmotic pressure corresponding to the concentration and hydrostatic pressure of the solution at the point considered. In other words, we may regard a semi-permeable membrane, such as is usually postulated in considering osmotic pressure, as being in reality a vapour-sieve, permeable only to the vapour. Such an assumption does not appear to be inconsistent with any of the well-established facts regarding osmotic pressure, and gives a somewhat simpler physical conception of the phenomena of osmosis.

Application of the Vapour-sieve Piston.

4. Without assuming that a vapour-sieve might be made to act as a semi-permeable membrane in osmotic experiments between solution and solvent, it is easy to show by the application of a vapour-sieve piston that the vapour-pressures of solution and solvent are the same (under any hydrostatic pressures) when they are in osmotic equilibrium through a semi-permeable membrane. Suppose that the solution and solvent are in equilibrium, as indicated in fig. 1, on either side of a semi-permeable membrane B under pressures P'' and P' applied by means of vapour-sieve pistons A and C. The pressure-difference $P'' - P'$ is the osmotic pressure P_0 . If the arrangement is contained in an isothermal enclosure, through which the vapour has free circulation, the vapour-pressure p'' of the solution under pressure P'' must be equal to the vapour-pressure p' of the solvent under pressure P' . Otherwise a continuous supply of work might be obtained by utilising the pressure-difference of the vapour. By similar reasoning we may assert generally that any two solutions in equilibrium through any kind of membrane or capillary surface must have the same vapour-pressures in respect of each of their constituents which are capable of diffusing through the surface of separation. This has for a long time been

* 'Phil. Trans.,' A, 1902, p. 147.

generally admitted, but the vapour-sieve piston supplies what is perhaps the simplest proof based on known physical properties.

We have seen that equation (3) must apply accurately to the equilibrium between a vertical column of solution and vapour under the action of gravity, but there is one respect in which the equilibrium of such a solution differs from that of the pure solvent. The concentration of the solution is independently variable, and must vary in such a manner as to make equation (3) hold. The variation of vapour-pressure with height in such a column of solution is not necessarily that due to variation of pressure alone. This has been recognised by Spens and Porter, who have deduced the variation with pressure independently of concentration, by the method of an isothermal cycle. The cycles which they employ appear, however, to be unnecessarily complicated. Porter applies pressure by means of an inert gas, which is assumed not to dissolve in the liquid or alter its vapour-pressure, and which adds unnecessary terms to the equation, besides requiring the

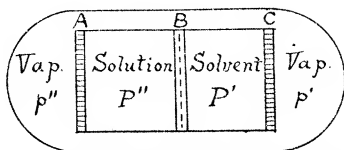


FIG. 1.—Equality of Vapour-pressure in Osmotic Equilibrium.

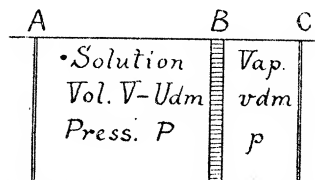


FIG. 2.—Change of Vapour-pressure of a Solution with Hydrostatic Pressure.

application of an additional piston permeable to the vapour but not to the gas. The result may be more simply and directly deduced by the aid of a vapour-sieve alone.

Imagine unit mass of solution of volume V , confined in a cylinder ABC between a fixed vapour-sieve B, and a solid piston A, by which pressure P is applied. The vapour, at pressure p , corresponding to P , is confined by a solid piston C, which we will suppose at first to be in contact with B, so that the volume of the vapour is initially zero. The cycle is as follows:—

(1) Keeping the pressures constant, evaporate a small mass dm of solvent. The work done by the piston C is $pv \, dm$. The work done on the piston A is $PU \, dm$, where U is the rate of diminution of volume of the solution at a pressure P per unit mass of solvent abstracted. The volume of solution remaining is now $V - U \, dm$. The state of the system at this stage is that represented in fig. 2.

(2) Increase the pressure on the solution to P' , by means of the piston A, at the same time moving the piston C, so as to keep the vapour in equilibrium with the solution without condensation. Suppose the pressure of the

vapour is increased to p' . The work done on the system is given by the expression,

$$-\int_P^{P'} P d(V - U dm) - \int_P^{p'} p dv dm.$$

(3) Keeping the pressures constant at P' and p' , condense the mass dm of vapour by moving piston C into contact with B, at the same time moving piston A outwards through a space $U' dm$, where U' is the value of U corresponding to pressure P' . The work done on the system is

$$-P'U' dm + p'v' dm.$$

(4) Release the pressure on the solution to its original value P , restoring the original volume V . The work done on the system is $+\int_P^{P'} P dV$.

Collecting the terms, and observing that $p'v' - pv = \int_P^{p'} p dv + \int_p^{p'} v dp$, we obtain finally,

$$\int_P^{P'} U dP = \int_p^{p'} v dp, \quad \text{or} \quad U dP = v dp, \quad (5)$$

which expresses the variation of vapour-pressure of a solution with pressure alone, assuming the temperature and concentration constant.

Variation of Concentration in a Vertical Column.

5. It appears from this result that the concentration of a vertical column of solution will not remain uniform when in equilibrium with the vapour at all heights, unless $U = V$ for the solution. If the whole length of the column is in contact with the vapour through a vapour-sieve envelope, the attainment of equilibrium with the vapour by condensation and evaporation would be comparatively rapid if the temperature is maintained uniform. If the solution were contained in an impervious tube, the same final result would be produced by diffusion of the vapour through the solution, but the attainment of equilibrium would be very slow.

Since the whole change of vapour-pressure in such a column in the equilibrium state is given by $v dp = V dP$, and the partial change dp' due to pressure is given by $v dp' = U dP$, the change dp'' due to change of concentration is given by $v dp'' = (V - U) dP$. If $V - U$ is negative, which is generally the case, the increase of vapour-pressure downwards in such a column will be less than that due to pressure alone, and the concentration will increase with depth. The values of $V - U$ for any solution are readily deduced from a table of densities or specific volumes V for any concentration C in grammes of solute per gramme of solution, by the relation

$$V - U = C(dV/dC), \quad (6)$$

which shows that $V - U$ is negative when the density increases with concentration.

Variation of Osmotic Pressure with Hydrostatic Pressure.

6. Since the osmotic pressure is the difference of the hydrostatic pressures P'' and P' of the solution and solvent when their vapour-pressures are equal, the variation of osmotic pressure with hydrostatic pressure is readily deduced from equation (5). If W is the specific volume of the pure solvent, we must have for equilibrium, $W dP' = U dP''$, since each is equal to $v dp'$. The corresponding change of osmotic pressure dP_0 is equal to the difference $dP'' - dP'$, whence,

$$dP_0/dP' = (W - U)/U, \quad \text{or} \quad dP_0/dP'' = (W - U)/W. \quad (7)$$

If $U = W$ there is no change in the osmotic pressure with hydrostatic pressure. This is equivalent to the assumption made by Lord Berkeley and Mr. Hartley* that the osmotic pressure varies with concentration only, which appears from their experiments to be approximately true for some solutions.

The relation between the equilibrium pressures P' and P'' for solution and solvent corresponding to the same value p_0 of the vapour-pressure is immediately obtained by integrating formula (5) between corresponding limits for solution and solvent. We have evidently,

$$\int_{p''}^{p'} U dP'' = \int_{p''}^{p_0} v dp, \quad \text{and} \quad \int_{p'}^{p''} W dP' = \int_{p'}^{p_0} v dp,$$

whence

$$\int_{p''}^{p'} U dP'' - \int_{p'}^{p''} W dP' = \int_{p''}^{p'} v dp, \quad (8)$$

where p', p'' are the vapour-pressures of solution and solvent, each under the pressure of its vapour only. This agrees precisely with the result obtained by Porter, but it seems better to deduce it from (5) in place of employing a special cycle.

The osmotic pressure may readily be deduced from the vapour-pressures p' and p'' , for any value of P' or P'' if the value of U is known. The most uncertain element in the calculation is the variation of U with pressure. If P_0' is the value of the osmotic pressure $P'' - P'$ when the solvent is under its own vapour-pressure p' only, or when $P' = p' = p_0$, the term containing W vanishes, and the limit of integration P'' is $P_0' + p'$. Similarly, if P_0'' is the osmotic pressure when the solution is under its own vapour-pressure p'' only, or when $P'' = p''$ and $P' = p'' - P_0''$, the term containing

* 'Roy. Soc. Proc.,' A, vol. 77, p. 156, 1906.

U vanishes. The limits of the integral $v dp$ are the same in both cases, and we obtain, assuming $v = R'\theta/p - c + b$,

$$(P_0' + p' - p'') U_0 = R'\theta \log(p'/p'') - (c - b)(p' - p'') = (P_0'' + p' - p'') W_0, \quad (9)$$

where U_0 , W_0 , are the mean values of U and W taken with respect to pressure between the corresponding limits of integration.

The term containing $(c - b)$ is retained, though unimportant at ordinary temperatures, because $(c - b)$ is about 75 times as large as W for water at 0°C. * and because it becomes important in comparison with $R\theta$ when p is large.

For most experimental purposes the small terms involving the factor $(p' - p'')$ may be neglected. We then have, approximately,

$$P_0' U_0 = R'\theta \log(p'/p'') = P_0'' W_0. \quad (10)$$

The values of P_0'' are the same for solutions having the same vapour-pressure p'' : or the values of the vapour-pressure will be very nearly the same for isotonic solutions tested under atmospheric pressure. But P_0'' cannot be directly measured by balancing against the pure solvent, as the corresponding value of the pressure on the solvent is large and negative, being approximately equal to $-P_0''$. The osmotic pressure measured by direct experiment, with the solvent under atmospheric pressure, is approximately equal to P_0' , and is correctly related to the vapour-pressure p'' of the same solution by equation (10), as was proved approximately by Spens, but more accurately by Porter.

For an actual vertical column of solution in equilibrium, equation (3) applies accurately, with V the specific volume of the solution in place of U . This gives the approximate equation usually quoted, namely,

$$P_0 V_0 = R'\theta \log(p'/p''), \quad (11)$$

where V_0 is the mean specific volume of the solution column, P_0 is the osmotic pressure *at the bottom* of the column, and p'' is the vapour-pressure at the top, where the concentration is generally different. Lord Berkeley and Mr. Hartley, in comparing their observations of vapour-pressure and osmotic pressure for the same solutions, found that the values of the osmotic pressure calculated from the vapour-pressure by equation (11) were much larger than those directly measured for the same solutions, and rightly attributed the discrepancy to variation of concentration in the imaginary

* Porter and Spens retain the term $U(p' - p'')$, but neglect the much larger term $(c - b)(p' - p'')$.

vertical column by which equation (11) is deduced. They therefore deduced the expression,

$$P_0''W_0 = R'\theta \log(p'/p''), \quad (12)$$

which correctly represents the relation between the osmotic pressure P_0'' and the vapour-pressure p'' of the solution *at the top* of such a column. In applying this equation to the conditions of their experiments, they made the assumption that the osmotic pressure could vary only with concentration, and that the value of P_0'' calculated from p'' by equation (12) for the osmotic pressure at the top of the column (where the solvent is under negative pressure) would be the same as the osmotic pressure directly measured for a solution of the same concentration with the solvent under atmospheric pressure. The approximate agreement of their observations with equation (12) would appear to imply, as Spens pointed out, that U is nearly equal to W for the solutions they employed. Strictly speaking, the value of P_0'' given by equation (10) or (12) is not equal to that of P_0' in equation (10), even if $U = W$ when solution and solvent are under the same pressure, because the mean values U_0 and W_0 are taken for positive and negative pressures respectively. The difference, however, would amount to less than 1 per cent. for the largest pressures measured by Lord Berkeley and Mr. Hartley.

Example of Variation of Concentration in a Vertical Column.

7. The variation of concentration in a vertical column of solution under gravity can be determined if the density and osmotic pressure are known as functions of the concentration. The osmotic pressure P_0 at the bottom of such a column given by equation (11) exceeds the value of P_0 , given by equation (10) for a solution having a composition corresponding to the normal vapour-pressure p'' , in the proportion of U_0 to V_0 . For strong solutions, the value of V_0 may be determined readily by successive approximation. But if the difference is small, and if the concentration C is defined as in equation (6), we have the approximate relation,

$$dC/C = -P(dV/dP)/V, \quad (13)$$

where dV is the change of V corresponding to the difference of osmotic pressures $dP = P_0 - P_0'$, and C , P , and V , are the mean values of the concentration, osmotic pressure, and specific volume for the column.

It may be interesting to give, as an example, the variation of concentration in a vertical column for the solutions examined by Lord Berkeley and Mr. Hartley, for which the requisite data are available. They give the concentration in grammes of sugar per litre of solution at 0° C. If the

concentration measured in this way is denoted by C' , while C denotes, as before, the concentration in grammes per gramme of solution, we have $C' = 1000 C/V$. The values of U and V for the solutions at 0° C. are calculated from Landolt and Bornstein's tables of the densities of cane-sugar solutions at 0° C., in which the concentration is expressed in grammes of sugar per 100 grammes of solution.

Table I.—Variation of Concentration in a Vertical Column of Solution of Cane-sugar at 0° C.

C' .	U .	V .	P_0' .	P_0 .	V_0 .	C_0' .	$C_0' - C'$.	Per cent.
760	0.986	0.775	134.0	172.0	0.767	900	140	18.4
660	0.990	0.795	101.0	126.0	0.787	741	81	12.3
540	0.993	0.825	67.5	82.0	0.817	600	60	11.1
420	0.996	0.858	44.0	51.5	0.852	460	40	9.5
300	0.998	0.895	26.8	30.2	0.897	325	25	8.3
180	0.999	0.932	14.0	15.1	0.930	193	13	7.3

The first four columns contain the data for the solutions employed, and correspond to the concentration at the top of the imaginary vertical column. P_0 and C_0' are the osmotic pressure and concentration at the bottom of the column. V_0 is the mean specific volume, which is seen to differ little from that at the top. The variation of concentration is considerable, and illustrates the order of error involved in applying the usual formula (12) to the case of strong solutions. The numbers in the last column appear to indicate a systematic error in the experimental numbers for strong solutions. They would be more regular if the theoretical expression given below for the osmotic pressure were employed in the calculation.

The Cellular Osmotic Column.

8. A case of special interest, as corresponding more closely with the kind of osmotic column which actually occurs in nature, is the cellular osmotic column. If a series of minute osmotic cells with flexible walls are disposed in a vertical column supported by fibrous material, and surrounded by an atmosphere of vapour, the hydrostatic pressure will be nearly uniform throughout the column, and equal to the vapour-pressure. Such a column will be in equilibrium when the concentration at any height is such that the vapour-pressure of the solution is equal to that in a column of vapour at the same height. Supposing that the vapour-pressure at the base is equal to that of the pure solvent, the concentration will increase from zero upwards, and the osmotic pressure referred to pure solvent at any height is that given

by equation (10). The concentration at any height is the same as that at the top of a continuous column of solution of the same height, but the elevation of the solvent is obtained more economically, without any excessive pressure differences, and with less than half the quantity of dissolved substance.

Since the osmotic pressure at any height depends on U , and not on V as in a continuous vertical column, it would appear at first sight as though the action of gravity in changing the concentration were eliminated by the cellular arrangement. But this is not the case, because the concentration in each little cell must vary in the same way as in a vertical column. The effect of this is to make the elementary difference of osmotic pressure between the top of one cell and the bottom of the next greater in the proportion of U to V than it would be if the concentration were uniform in each cell. Since the direction of the change of concentration in each cell depends on the direction of gravity, it would appear that gravity must exert some directive action on the growth of the plant on this account. In a growing plant the conditions are seldom those of equilibrium or constant temperature, and many other factors are operative, but the consideration of the condition of equilibrium is important, because the rate of osmosis will be determined chiefly by the extent of the departure from the condition of equilibrium.

Method of the Osmotic Circuit.

9. A circuit consisting of different phases containing one component in common presents many points of analogy with an electric circuit. The analogy is particularly close between thermoelectric and osmotic circuits. The electromotive force round a circuit is measured by the work done in taking unit quantity of electricity round the circuit, and is zero in a thermoelectric circuit when there is no difference of temperature. Similarly, in an osmotic circuit in equilibrium at uniform temperature, the work done in taking unit mass of solvent round the circuit must be zero. Neglecting external forces, such as gravity, the work done is represented by the integral of $U dP$ taken round the circuit between limits corresponding to the transition points between the phases, where U is the increase of volume of the phase considered per unit mass of solvent added at a pressure P . The method of the osmotic circuit essentially corresponds to the more familiar method of the isothermal cycle, but it has the advantage that the limits of integration are obvious, and that the correct result can be written down in any case by mere inspection; whereas the method of the isothermal cycle is often very complicated and difficult to follow, as may be seen by reference to the

examples given by Spens and Porter. A number of unnecessary terms are introduced, and the greatest care is required to avoid making mistakes, of which a large number might be cited.

If we consider a vertical column of liquid or solid, in equilibrium with its vapour through a vapour-sieve envelope as in Section 2, taking the integral of $v dp$ round any circuit partly in the vapour and partly in the liquid or solid, we obtain immediately equation (3) and its corresponding integral. In the case of a pure liquid, the work done against gravity is negligible, because U is the same as V , the specific volume of the liquid, at all points. In the case of a solution, where U may differ from V , the work done against gravity in raising a mass of specific volume U through a solution of specific volume V , which is represented by the integral of $(V-U)dP$ per unit mass, must be added to the integral of UdP in the solution. This has the effect of replacing U by V in the equation, as already explained in Section 5, and takes account of the effect of gravity in altering the concentration. If this effect of gravity is neglected, and the solution assumed uniform, the method naturally gives the effect of pressure alone, as represented by equation (5).

Analogy with the Isothermal Cycle.

10. A closer correspondence between the circuit method and the method of the isothermal reversible cycle is obtained if we suppose the pressure-differences in the circuit utilised for the performance of external work by means of imaginary isothermal reversible motors or pumps. Let fig. 3

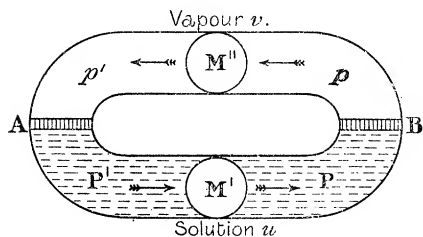


FIG. 3.—Osmotic Circuit, giving Variation of Vapour-pressure of Solution with Hydrostatic Pressure P .

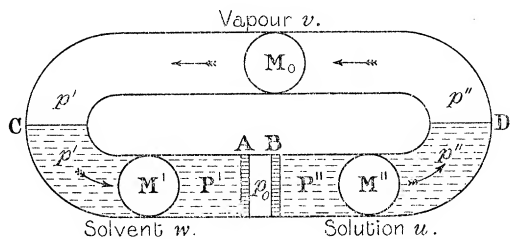


FIG. 4.—Osmotic Circuit for Solvent, Solution, and Vapour.

represent such a circuit consisting of solution and vapour separated by vapour-sieve partitions A and B. Suppose isothermal reversible motors M' , M'' , included in the circuit, separating the solution into two parts under pressures P and P' , and the vapour into two parts under corresponding pressures p and p' . If the temperature is maintained uniform, the work done by the motor M' per unit mass of solvent passing through it must be

equal and opposite to that done by the motor M'' . No external work is done at other points of the circuit. The work done per unit mass passing through the motor M' is evidently

$$P'U' + \int_{P'}^P P dU - PU = \int_P^{P'} U dP. \quad (14)$$

Similarly the work done per unit mass of the vapour passing through the motor M'' in the direction indicated by the arrows is given by $\int_{p'}^p v dp$. The sum of these must be equal to zero, which corresponds with the result of the isothermal cycle represented by equation (5).

As an additional complication, we may introduce the solvent into the circuit (though this is really unnecessary, and does not prove anything new), as indicated in fig. 4, by supposing it separated from the solution by a semi-permeable membrane under pressures P' and P'' respectively, such that $P' - P''$ equals the osmotic pressure P_0 . An equivalent method is to employ a pair of vapour-sieve partitions A and B, separated by a space containing vapour at the common pressure p_0 . The motors M', M'' serve to reduce the pressures of the solvent and solution respectively to equilibrium with their normal vapour-pressures p', p'' . The vapour is separated into two parts at pressures p' and p'' by the motor M_0 . Equating to zero the sum of the external work done by the three motors, we have evidently,

$$\int_{p''}^{p'} U dP + \int_{p'}^{p''} v dp + \int_{P'}^{P''} W dP = 0. \quad (15)$$

This corresponds with the isothermal cycle worked out by Porter,* but the circuit method enables the whole process to be displayed graphically, and the physical interpretation of each term in the result is made immediately obvious.

Effect of Pressure on the Latent Heat of Vaporisation.

11. In an isothermal circuit or cycle the algebraic sum of the quantities of heat absorbed and liberated must also be equal to zero. Applied to the isothermal circuit of fig. 1, in which solvent and solution are in osmotic equilibrium under pressures P' and P'' , this condition leads to the result that the latent heat of vaporisation of the solution at A must be equal to the latent heat of condensation of the solvent at C, under the same vapour-pressure plus the heat Q_0 evolved on dilution at B.

$$L'' = L' + Q_0. \quad (16)$$

Applied to the osmotic circuit of fig. 3, the condition gives the rate of

* *Loc. cit.*

variation of the latent heat of vaporisation of a solution with change of pressure at constant temperature. The heat absorbed in vaporisation at A, plus the heat absorbed in the motor M'' , equals the heat evolved in condensation at B, plus the heat evolved in the motor M' . Supposing for convenience that the difference of pressure is small, or that $P' - P = dP$, and $p' - p = dp$, the heat absorbed in the motor M'' is $-\theta dp (dv/d\theta)$, which is approximately equal to the work done $-v dp$, since $(dv/d\theta)$ is nearly equal to v/θ for the vapour. The heat absorbed in the motor M' is similarly equal to $-\theta dP (dU/d\theta)_p$. Since $v dp = U dP$, we have evidently the relation,

$$(dL/dP)_\theta = U - \theta (dU/d\theta)_p. \quad (17)$$

A precisely similar relation applies for the pure solvent, with the substitution of W , the specific volume of the pure solvent, in place of U . If we apply this relation to the case of water at 4°C ., at which temperature $(dW/d\theta) = 0$ under atmospheric pressure, we find the rate of increase of the latent heat per atmosphere (10^6) of pressure equal to 10^6 ergs, or a pressure of about 42 atmospheres would be required to increase the latent heat by 1 calorie. The change at other temperatures can be deduced from a knowledge of the coefficient of expansion.

Theory of Osmotic Pressure.

12. The several theories of osmotic pressure now current may be roughly classified under four heads: (1) The gas-pressure theory, according to which the osmotic pressure due to the molecules of the solute is the same as that which would be exerted by the same number of molecules of gas occupying the same volume at the same temperature. (2) The surface-tension theory, according to which the pressure developed is due to surface-action or difference of surface-tension. (3) The association, or hydrate theory, according to which the effects are due to residual chemical affinity between solvent and solute, resulting in the formation of hydrates or similar molecular complexes. (4) The vapour-pressure theory, according to which the osmotic pressure is simply the pressure required to produce equilibrium of vapour-pressure between the solvent and solution. It is probable that all the theories possess some elements of truth, and that they may be to some extent merely different aspects of the same phenomenon.

As an illustration of the deviation of the experimental results from the usually accepted theory, the observations of Lord Berkeley and Mr. Hartley on the osmotic pressures of strong solutions of cane-sugar and dextrose at 0°C . are plotted in the accompanying diagram, fig. 5. In their papers the results are tabulated and plotted in terms of concentration C' in grammes

of sugar *per litre of solution*, which has generally been adopted in dealing with osmotic pressure in consequence of Van't Hoff's theory. It is more convenient, however, in dealing with osmotic pressures or depressions of the freezing-point in strong solutions, to plot the results in terms of concentration C'' expressed in grammes of solute per gramme of solvent, because for normal solutions such as cane-sugar the curves are more nearly straight, and the deviation of the observations from the theoretical curves can be

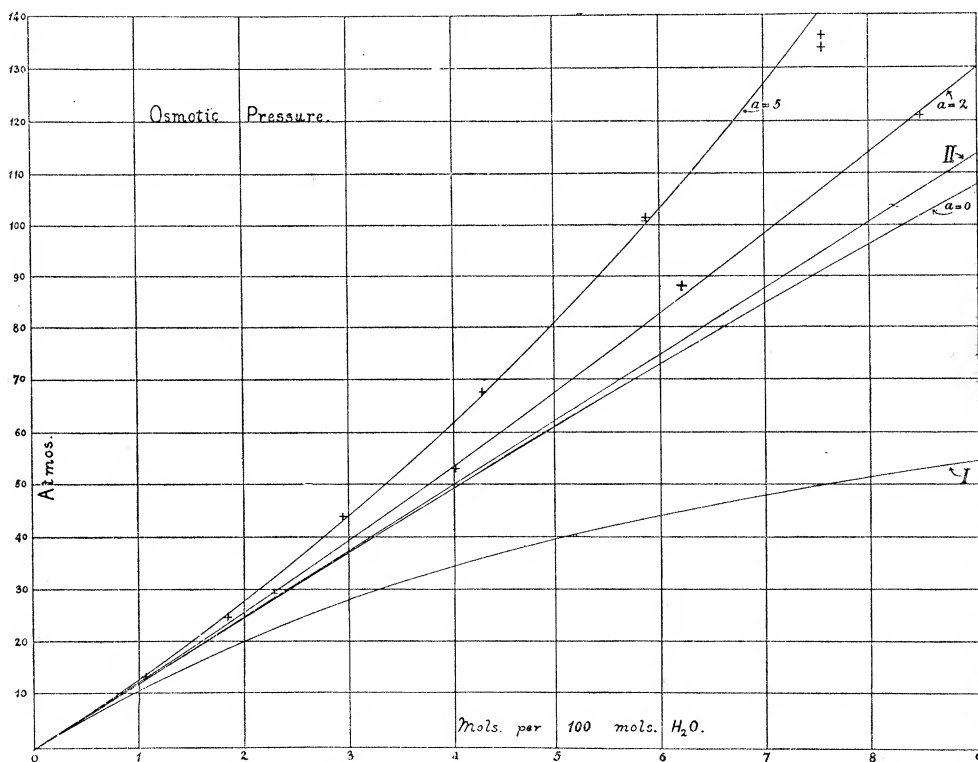


FIG. 5.—Osmotic Pressures of Solutions of Cane-sugar and Dextrose.

more readily estimated. In dealing with densities or specific volumes it is generally better to employ the percentage concentration 100 C (grammes of solute per 100 grammes of solution) in terms of which they are usually tabulated. The relation between the three modes of expressing the concentration is

$$C'V = C = C''/(1+C'').$$

In comparing solutions of different substances it is necessary to plot the results in terms of the ratio of the number of molecules n of the dissolved substance to the number of molecules N of the solvent in the solution,

because the relations involved are of a molecular nature. We have $n/N = mC''/M$, where m and M are the molecular weights of solvent and solute respectively. In plotting the observations in fig. 5, N is taken as equal to 100, and the values of the osmotic pressure are plotted against the number n of molecules of solute to 100 molecules of solvent. The molecular weight of water is taken as 18, and the corresponding values for cane-sugar and dextrose as 342 and 180 respectively, which are sufficiently approximate for the purpose.

According to the gas-pressure theory, as usually stated, the pressure exerted should be given by the formula,

$$P = R\theta C'/M = R\theta C/MV, = R\theta C''/MV (1 + C''), \quad (18)$$

where R is the gas-constant and V the volume of unit mass of solution containing C/M gramme-molecules of solute. It is well-known that this gives values of P which are much too small for strong solutions, in fact nearly three times too small for the strongest solutions of cane-sugar tested by Lord Berkeley and Mr. Hartley, as shown by the curve marked I in fig. 5. A better approximation is obtained if V is replaced by the volume of solvent in the solution, namely $(1 - C) U$, which gives

$$P = R\theta C/MU (1 - C) = R\theta C''/MU. \quad (19)$$

This proceeding is analogous to subtracting the covolume term b from the volume occupied, as in the gas equation of Van der Waals. But even this is not sufficient in the case of cane-sugar, as shown by the straight line marked II in fig. 5. The residual discrepancy may be accounted for by introducing other empirical terms in the equation as indicated by Lord Berkeley in his note *On the Application of Van der Waals' Equation to Solutions*.^{*} This is not altogether satisfactory, because so many different types of equation are possible, and the empirical constants cannot be interpreted, or predicted from other properties of the substances concerned.

The surface-tension and hydrate theories, as usually stated, are unprofitable, because they do not appear to admit of the calculation of the osmotic pressure for comparison with the results of experiment. There is no doubt that differences of surface-energy exist between the solution and solvent, and that molecular complexes are formed in solution, and that such effects might give rise to a difference of pressure, but the relation between the phenomena is not directly capable of numerical expression in any obvious manner.

The vapour-pressure theory is undoubtedly the most practical, because there is a definite and simple relation between the vapour-pressure and the

^{*} 'Roy. Soc. Proc.,' A, vol. 79, p. 125.

osmotic pressure, which has been closely verified by the experiments of Lord Berkeley and Mr. Hartley for strong solutions. It remains to be seen whether the vapour-pressure of a solution can be theoretically related in any simple manner to its molecular constitution. A step in this direction has been made by Poynting,* who supposes that each molecule of the solute combines with a molecules of solvent in such a manner as to render them inactive for evaporation. If there are n molecules of solute to N of solvent in the solution, the ratio of the vapour-pressures p''/p' of solution and solvent should in that case, according to Poynting, be the ratio of the number of free molecules of solvent $N-an$ to the whole number of molecules of solvent N in the solution. We thus obtain the relations

$$p''/p' = (N-an)/N, \quad \text{or} \quad (p' - p'')/p' = an/N. \quad (20)$$

In order to reconcile this assumption with Raoult's law for dilute solutions of non-electrolytes, it is necessary to suppose that $a = 1$, or that each molecule of solute combines with only *one* molecule of solvent. Since $n = C/M$ and $N = (1-C)/m$, where M, m are the molecular weights of the solute in solution and of the vapour of the solvent respectively, we obtain immediately by substitution in (2) or (3), putting $v = R\theta/np$ and $V = U$, the approximate result (19), which is equivalent to that given by Poynting. But Poynting applies the assumption only to dilute solutions, and does not, therefore, distinguish between U, V , and W .

The advantage of making this assumption with regard to the variation of the vapour-pressure with the number of free molecules is that it gives a comparatively simple explanation, without straining the gas-pressure analogy, of the fact that the osmotic pressure appears to depend more nearly on the volume occupied by the solvent in the solution than on the whole volume of the solution. The particular assumption made does not, however, appear to be quite satisfactory for two reasons: (1) it does not represent the results of experiment sufficiently closely for strong solutions, and (2) it is necessary to suppose that each molecule combines with only *one* molecule of solvent. If each molecule of the solute combines with two or three or more molecules of solvent, the change of vapour-pressure and the depression of the freezing-point, on Poynting's assumption, would be twofold or threefold, or in proportion to the number of molecules to each molecule of solute. At first sight this would give a natural explanation on the association theory of the case of electrolytes, if there were not so much conclusive evidence that the effect in this case is due to dissociation or multiplication of molecules. The existence of multiple hydrates would rather lead one to expect that the molecular

* 'Phil. Mag.' vol. 42, p. 298, 1896.

complexes occurring in solutions often contain several molecules of solvent, and that the number of molecules of solvent in each complex may vary considerably without producing so marked an effect on the vapour-pressure or the freezing-point as would be indicated by Poynting's theory.

A more natural assumption to make with regard to the dependence of the vapour-pressure on the number of molecules in the solution would appear to be that the vapour-pressure ratio p''/p' is equal to the ratio of the number of free molecules of solvent to the whole number of molecules in the solution, instead of to the number of molecules of solvent. On this view, each molecular complex is treated as a single molecule, and it is immaterial, to a first approximation, how many molecules of solvent it may contain. If each molecule of solute appropriates a molecules of solvent, and if n , N denote, as before, the whole number of molecules of solute and solvent respectively in the solution, the number of free molecules of solvent is $N-an$, and the whole number of molecules in solution is $N-an+n$. We thus obtain,

$$\begin{array}{ll} \text{Ratio of Vapour-Pressures} & \dots\dots\dots p''/p' = (N-an)/(N-an+n), \\ \text{Relative Lowering of Vapour-Pressure} & (p'-p'')/p' = n/(N-an+n), \\ \text{Lowering Relative to Solution} & \dots\dots\dots (p'-p'')/p'' = n/(N-an). \end{array} \quad (21)$$

This agrees with Poynting's assumption in the special case where $a = 1$, and coincides with Van't Hoff's theory in the limit for dilute solutions, *whatever be the value of a* . But it makes a very considerable difference in the case of strong solutions. In applying the assumption $p'/p'' = (N-an+n)/(N-an)$ to strong solutions, it is necessary to employ the logarithmic formula (10), namely, $P_0' U_0 = R\theta \log_e(p'/p'')/m$, in place of the approximate formula (2). The curves in fig. 5 are drawn to represent the values of the osmotic pressure for the two cases $a = 2$ and $a = 5$, which appear to represent the observations on dextrose and cane-sugar within the limits of experimental error. The product PU is plotted in place of P , because the correction for U is small and somewhat doubtful, and was not applied by Lord Berkeley and Mr. Hartley. The highest points for cane-sugar at $n = 7.6$ lie below the curve, but the agreement is sufficiently close to suggest that the formation of molecular complexes containing several molecules of solvent is a very probable explanation of the main features of the variation of osmotic pressure with concentration in solutions of the same kind as those of cane-sugar.

It will be observed that since $\log_e(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 \dots$, the expression for the osmotic pressure reduces approximately to the form

$$P = R\theta n/(N-an) Um, \quad (22)$$

when n is small compared with $N-an$. Here Um is the volume occupied by 1 gramme-molecule of the solvent in the solution; $N-an$ is the number of free molecules of the solvent in the solution to n of the solute. The osmotic pressure is therefore approximately equal to that which would be exerted by n molecules of gas in the volume occupied by the remaining free molecules of the solvent. The gas-pressure analogy still holds to this extent as a first approximation, even in fairly strong solutions. But it would be straining the analogy unduly to regard the pressure which the molecules would exert in an imaginary volume if they were gaseous as being the primary cause of the phenomena of osmotic pressure. In reality the equilibrium depends primarily on equality of vapour-pressure. If vapour is supplied to a solution at a pressure in excess of the normal vapour-pressure of the solution, the vapour will condense in the solution, and the condensation will continue until either the pressure, or the temperature, or the concentration of the solution, is changed in such a manner as to restore equilibrium between the solution and the vapour. The assumption of a simple molecular relation for the vapour-pressure seems also to give better agreement with experiment than the assumption of a similar relation for the gas-pressure.

Lowering of the Freezing-point in Strong Solutions.

13. Direct measurements of the vapour-pressure or osmotic pressure in strong solutions are very difficult, and there is little material available for testing the theory in this direction. Observations of the lowering of the freezing-point are more numerous, and less liable to serious error, although they present considerable difficulties in the case of strong solutions. In the usual case of the solvent separating out in the pure state on freezing, the vapour-pressure of the solution at the freezing-point must be equal to that of the solid solvent. Taking the case of aqueous solutions for simplicity of description, in order to find the osmotic pressure of a solution at its freezing-point we have merely to substitute the value p of the vapour-pressure of ice in place of p'' , the vapour-pressure of the solution in formula (10) for the osmotic pressure. The determination of vapour-pressure, or molecular weight, or osmotic pressure, by the freezing-point method depends, therefore, primarily on knowing the relation between the vapour-pressures of ice and water below the freezing-point.

The difference of vapour-pressures $p-p'$ of ice and water at a temperature t° C. near the freezing-point 0° C. is generally obtained from Kirchhoff's approximate formula,

$$dp/d\theta - dp'/d\theta = L/\theta v, \quad (23)$$

where L is the latent heat of fusion, and v the volume of the vapour. Putting $p-p'$ for $dp-dp'$, and t for $d\theta$, and substituting $v = R\theta_0/mp'$, we obtain,

$$(p-p')/p' = +mLt/R\theta_0^2. \quad (24)$$

Equating this to the approximate formula for the relative lowering of the vapour-pressure of the solution $(p'-p'')/p'$ in terms of the osmotic pressure and the concentration, we have the usual relation

$$mPU/R\theta = n/N = mC''/M = -mLt/R\theta_0^2 = -2.64t/\theta_0. \quad (I)$$

This gives for the "molecular lowering" of the freezing-point produced by 1 gramme-molecule of solute in 100 grammes of solvent, in the case of water, the value $t_m = 18^\circ.6$, or for 1 gramme-molecule in 100 *gramme-molecules* of water the value $t = 1^\circ.033$, if L is taken as 79.5 calories, and $R = 1.98$ calories.

Results for the lowering of the freezing-point in strong solutions are generally compared by tabulating the molecular lowering deduced from different ranges of temperature, for comparison with the approximate result given by this formula. This method illustrates the wide divergence of the experimental results from the approximate formula, but it does not throw much light on the causes of the divergence, because the approximate formula deduced on such assumptions could not be expected to hold at all accurately except in the immediate neighbourhood of the freezing-point.

The formula tacitly assumes that the ratio of the difference of vapour-pressures of ice and water to the vapour-pressure of water is directly proportional to t . To give some idea of the error involved in the case of strong solutions, the values of $\log_e (p'/p)$ calculated on this assumption are tabulated under the heading I in the accompanying Table II, for comparison with the values given by more accurate formulæ.

A method adopted in many books is to integrate Kirchhoff's equation on the assumption that the latent heat of fusion L , or rather the difference of the latent heats of vaporisation of the solid and liquid, is constant, which leads at once to the result,

$$\log_e (p'/p) = -mLt/R\theta\theta_0, = -2.64t/\theta. \quad (II)$$

This fits very well with formula (10) for the osmotic pressure, giving the simple expression $PU = Lt/\theta_0$, but since the specific heats of water and ice are known to differ considerably, the values to which it leads are probably quite as much in error as those deduced on the first assumption. The resulting values of $\log_e (p'/p)$ are given in the table under the heading II, and are seen to differ from those given by I by about 8 per cent. at -10°C . and about 16 per cent. at -20°C . The equation is no doubt preferable to I

as corresponding to a simple and definite assumption, but as the assumption is certainly wrong, it would be futile to apply the equation to strong solutions.

Accurate Equation for the Vapour-pressures of Ice and Water in terms of the Specific Heats.

14. In order to obtain a more accurate equation it is necessary to take account of the difference of the specific heats, which corresponds to the variation of the latent heat of fusion. This may be done in many ways, but it affords a good example of the circuit method. Imagine a circuit consisting of parallel columns of ice and water, AB, CD, in equilibrium at either end with vapour at 0°C ., and vapour at $-t^\circ\text{C}$., as indicated in fig. 6. Suppose

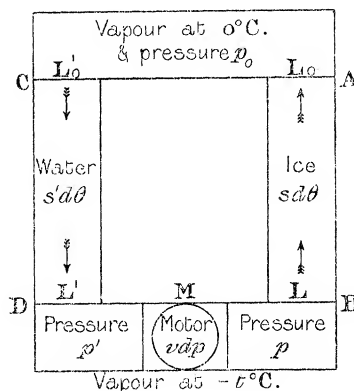


FIG. 6.—Circuit Method for Ratio of Vapour-pressures of Ice and Water in terms of the Specific Heats.

unit mass to travel round the circuit in the direction indicated, starting with the state of vapour at 0°C . under the vapour pressure p_0 , which is the same for ice and water. Heat L'_0 is evolved in condensation to water at 0°C . Heat $s'd\theta$ is evolved in cooling for each element $d\theta$ from 0° to $-t^\circ$, where s' is the specific heat of water under vapour-pressure p' . Heat L' is absorbed in evaporation at $-t$ at a pressure p' . The vapour is then expanded through a motor M at constant temperature $-t$ to a pressure p , the vapour-pressure of ice at $-t$. The work done in the motor is the integral of $v dp$, and is equal to the heat absorbed. Heat L is evolved in condensation to ice at $-t$. The integral of $s d\theta$ is absorbed in heating to 0°C ., where s is the specific heat of ice under its own vapour-pressure p . Finally, heat L_0 is absorbed in evaporation at 0°C . The work done by the expansion of the solid or liquid may be neglected, because the pressures are very low and the volumes of the solid and liquid are quite negligible compared with that of the vapour.

By the first law, equating the heat absorbed to the work done, we obtain,

$$(L-L')-(L_0-L'_0) = \int_{\theta_0}^{\theta} (s'-s) d\theta. \quad (25)$$

By the second law, taking the integral of dH/θ round the circuit,

$$(L-L')/\theta-(L_0-L'_0)/\theta_0 = \int_{\theta_0}^{\theta} (s'-s) d\theta/\theta + \int_p^{p'} v dp/\theta. \quad (26)$$

Substituting from (25) in (26) for $L-L'$, and putting L_f the latent heat of fusion at 0° C., for the difference of the latent heats of vaporisation at 0° , we obtain the required relation in terms of L_f and the specific heats.

$$R \log_e (p'/p)/m = -L_f t/\theta\theta_0 + \frac{1}{\theta} \int_{\theta_0}^{\theta} (s'-s) d\theta - \int_{\theta_0}^{\theta} (s'-s) d\theta/\theta. \quad (27)$$

This result is equivalent to equation II with added terms representing the effect of the difference of the specific heats. The integrals cannot be evaluated exactly without a knowledge of the mode of variation of the specific heat with temperature, but we shall evidently obtain a much better approximation than either I or II if we assume $(s'-s)$ constant and equal to its value at 0° C. The most probable value of the difference of the specific heats of ice and water at 0° C. appears to be $(s'-s)=0.52$. Putting $L_f=79.5$, $R/m=0.1103$, and $\theta_0=273$, we obtain the numerical formula,

$$\log_e (p'/p) = -2.64t/\theta + 4.71(t/\theta - \log_e (\theta/\theta_0)). \quad (III)$$

The first term is the same as in II. The second term, depending on the specific heats, is small because t/θ is nearly equal to $\log_e (\theta/\theta_0)$ when t is small. Its value to a first approximation is $-2.35(t/\theta_0)^2$. Values deduced from this formula are given in column III. They lie nearly midway between those given by I and II.

The mode of variation of the specific heat of water at temperatures below 0° C. cannot be determined satisfactorily by experiment. It probably increases with fall of temperature, being continuous with the curve above 0° C. The specific heat of ice appears to diminish with fall of temperature. Regnault finds the value $s=0.462$ for ice (corrected) between 0° and -78° C. Nordmeyer and Bernoulli give 0.345 between 0° and -185° . The probable error involved in neglecting the variation of the specific heat is small, and can be estimated by making different assumptions. If we suppose for instance that the difference of the specific heats varies *directly* as the absolute temperature, or that $(s'-s)=s_0\theta/\theta_0$, we obtain the simple result,

$$R \log_e (p'/p)/m = -L_f t/\theta\theta_0 - s_0 t^2/2\theta\theta_0. \quad (28)$$

If $s_0=0.52$, this gives the numerical formula,

$$\log_e (p'/p) = -2.64t/\theta - 0.0172t^2/2\theta. \quad (IV)$$

If, on the other hand, we make the exactly opposite assumption, that $(s' - s)$ varies *inversely* as θ , or $s' - s = 0.52\theta_0/\theta$, we obtain the equation,

$$\log_e(p'/p) = -2.64 t/\theta - 4.71 (t/\theta - (\theta_0/\theta) \log_e(\theta/\theta_0)). \quad (V)$$

Values calculated by these formulæ are given in columns IV and V. The differences from column III are probably within the limits of error of our knowledge of the specific heats at 0° C. The absolute value of $(s' - s)$ is more important for our purpose than a knowledge of the mode of variation.

It will be observed in comparing the values of $\log_e(p'/p)$ in columns III, IV, and V, with the values of $-2.64 t/\theta_0$ given in column VI, that they are very nearly equal; the differences average about 0.5 per cent. down to -50° C. The values are all very nearly proportional to t , at least within the limits of possible error of our knowledge of $(s' - s)$. If we might assume $s_0 = 2L_f/\theta_0 = 0.582$, in (28), or $(L - L')/\theta^2 = L_f/\theta_0^2$, the equation would reduce *exactly* to the very simple form

$$\log_e(p'/p) = -2.64 t/\theta_0, \quad (VI)$$

which is the same as II, except that θ is replaced by θ_0 . This requires a rather smaller value for the specific heat of ice than that usually accepted, but considering the uncertainty of our knowledge of the specific heats, this formula has been adopted in the calculations for the sake of simplicity, as it has a definite theoretical basis, and agrees with III or IV within the probable limits of error of experiment. In many cases formula V, which allows for the probable increase of $(s' - s)$ with fall of temperature, appears to give better agreement with experiment, and it may eventually prove to be a better approximation than the simpler formula VI.

Table II.—Values of $\log_e(p'/p)$ for Ice and Water according to Formulæ I—VI.

t.	I.	II.	III.	IV.	V.	VI.	(p'/p).
°							
— 2	0.01915	0.01948	0.01935	0.01935	0.01935	0.01934	1.01953
— 5	0.04721	0.04924	0.04842	0.04843	0.04842	0.04835	1.04955
— 7	0.06548	0.06948	0.06787	0.06790	0.06786	0.06769	1.07004
—10	0.09229	0.10037	0.09705	0.09711	0.09701	0.09670	1.10154
—13	0.11840	0.13200	0.12631	0.12638	0.12622	0.12571	1.13397
—15	0.13543	0.15348	0.14581	0.14596	0.14567	0.14505	1.15611
—20	0.17680	0.20870	0.19470	0.19500	0.19440	0.19340	1.21340
—30	0.25463	0.3259	0.2927	0.2939	0.2914	0.2901	1.33660
—40	0.3269	0.4535	0.3913	0.3945	0.3876	0.3868	1.47231
—50	0.4944	0.5930	0.4896	0.4963	0.4828	0.4835	1.62181
—60	0.4575	0.7435	0.5858	0.5977	0.5719	0.5802	1.78649

The last column contains the value of the ratio of the vapour-pressures of water and ice required for calculating the lowering of the freezing-point by the rule for the vapour-pressure of a solution given in equations (21). It may be remarked that this ratio cannot be taken from tabulated values of the vapour-pressures of water and ice, such as those given in Landolt and Börnstein's tables (based partly on the work of Thiesen and Scheel), because the vapour-pressures of water below the freezing-point cannot be determined experimentally with sufficient accuracy for the purpose, since the difference of vapour-pressure is very small. Thus the ratio of the vapour-pressures at -2° C. from the tables is 1.0164, and the required difference 0.0164 is about 15 per cent. too small. But the tabulated vapour-pressures for ice agree with those calculated by the author's method* to within a few thousandths of a millimetre, on the assumption that its specific heat is 0.48 and equal to that of steam.

Application to Non-Electrolytes.

15. In order to apply this table to the lowering of the freezing-point of a solution, the values of $p'/p - 1$, taken from the last column, multiplied by 100, are plotted against the corresponding values of t in the diagram, fig. 7, and give the curve marked $a = 0$. The same curve, if the abscissa is taken to represent n , the number of molecules of solute to $N = 100$ of solvent, should give the depression of the freezing-point for a solution for which $(p' - p'')/p'' = n/N$, that is to say for the case in which $a = 0$ in equations (21), or the solute does not combine with any molecules of solvent. The curves for different values of a are found from the curve $a = 0$ by calculating the values of the ratio $(p' - p'')/p'' = n/(N - an)$, finding the corresponding values of t from the vapour-pressure curve $a = 0$, and plotting the values so found against n .

The straight line $t = -1.033n$ is the tangent at 0° C. to the vapour-pressure curve $a = 0$, and represents the value of the depression of the freezing-point for a normal substance according to Van't Hoff's cryoscopic constant $k = 18^{\circ}.6$ for 1 molecule of solute in 100 grammes of solvent. It gives a fair approximation to the curve of vapour-pressure for weak solutions, the error at $t = -10^{\circ}$ being less than 5 per cent. It may be necessary to point out that this assumption differs widely from the assumption of a cryoscopic constant for *volume-normal* solutions (gramme-molecules per litre) which is often made in reducing freezing-point observations according to the gas-

* 'Roy. Soc. Proc.,' June, 1900. The vapour-pressures of water below the freezing-point are often calculated from Regnault's formula for the latent heat, which appears (*loc. cit.*) to be inaccurate.

pressure theory. The curve so obtained depends on the density of the solution, and is different for different substances. If the depression of the freezing-point for solutions of cane-sugar were proportional to the number of gramme-molecules per litre, we should obtain the curve marked I in fig. 7, which illustrates the danger of pushing an attractive analogy too far. The depression calculated on the gas-pressure theory would be $3^{\circ}72$ for a solution containing 2 gramme-molecules of sugar per litre, as against $6^{\circ}6$ if the depression is

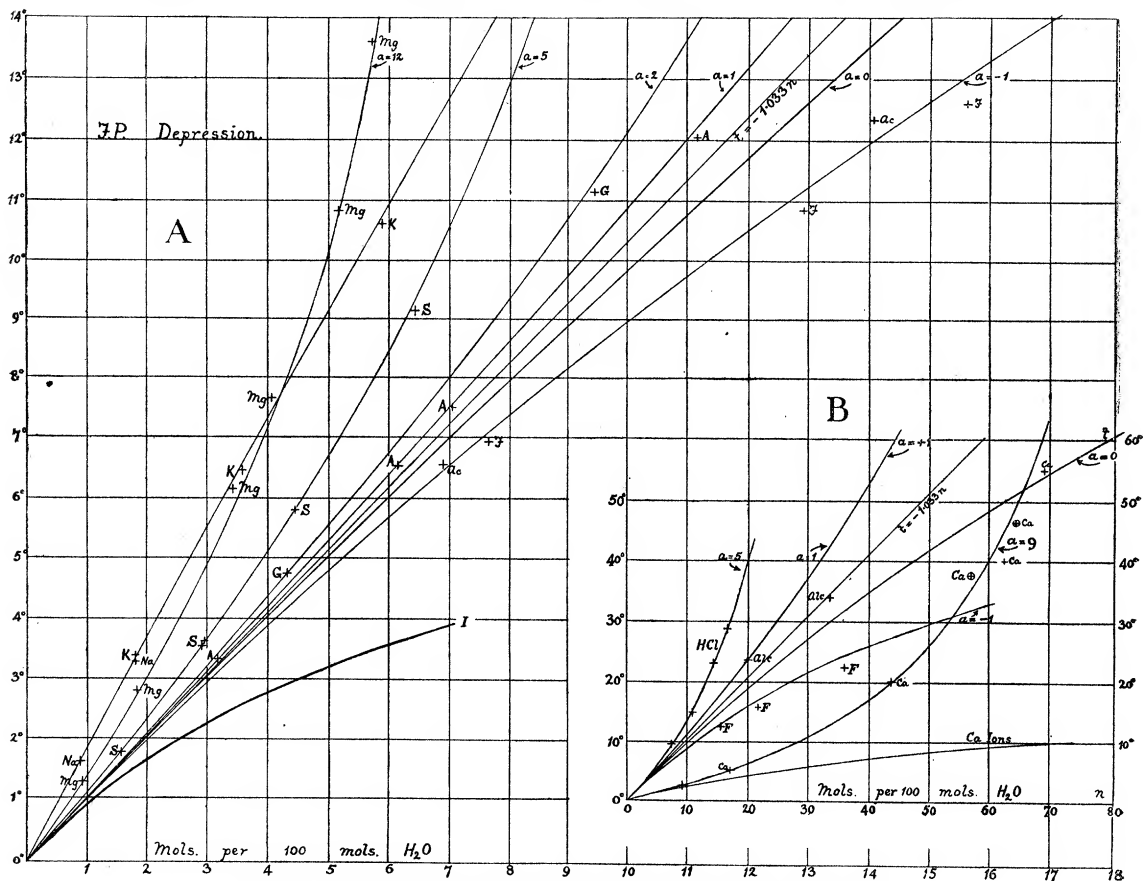


FIG. 7.—Depression of the Freezing-point in Aqueous Solutions.

proportional to n/N . Experiment gives $9^{\circ}15$, according to Jones and Getman. The gas-pressure theory is inconvenient, because it involves considerations of density, and it fails to represent the observations satisfactorily, even for weak solutions, because it gives in many cases so bad an approximation to the vapour-pressure curve.

The crosses marked S, representing the observations on the depression of the freezing-point for cane-sugar, agree very well with the curve marked

$a = 5$, as in the case of the osmotic pressure. Thus the observed depression at $n = 6.41$ is $t = -9^{\circ}15$. The calculated value for $a = 5$ is $t = -9^{\circ}30$. Van't Hoff's rule gives $t = -6^{\circ}60$. For $a = 0$ the depression would be $t = -6^{\circ}42$. The depressions recorded in Landolt and Börnstein's tables for methyl and ethyl alcohols, marked A in fig. 7A, agree very well with the curve marked $a = 1$, up to $n = 20$ molecules per 100 of solvent. One observation for ethyl alcohol in fig. 7B, at $n = 33.7$, lies entirely off the curve.

[*Note added April 13, 1908.*—Guthrie's observations* on the freezing of alcohol solutions appear to indicate that a hydrate may separate in place of pure ice when $n = 20$, giving rise to a discontinuity in the F. P. curve. Analysis of his observations down to -65° C. indicates a third branch extending from $n = 42$ to $n = 90$, but the temperatures in this region are probably not very accurate. The ice branch, giving $a = 1$, can be traced as far as $n = 25$, in the absence of the first hydrate.]

The values for glycerine (G) agree with the curve marked $a = 2$. The freezing-points for acetone (Ac) and formic acid (F) lie *below* the curve $a = 0$, in a manner which suggests that the dissolved molecules associate with each other in solution according to a similar law, as the points representing the observations lie very symmetrically on either side of the curve marked $a = -1$.

Application to Electrolytes.

16. In applying the theory to electrolytic solutions, we are met by the difficulty that the molecules are dissociated to a variable extent depending on the dilution. The degree of dissociation is usually inferred from the ratio of the molecular electric conductivity of the solution to that at infinite dilution. It is very doubtful what this ratio really represents in the case of strongly dissociated electrolytes, as the free ions are so numerous that they must interfere very greatly with each others' movements. It is possible that the dissociation is really much greater than that calculated in this manner, but the ratio may nevertheless represent the *effective* number of free molecules from the point of view of depression of the freezing-point as well as from the point of view of electric conductivity. Adopting this hypothesis, if $n'' = (1 + k/k_0)n$ is the effective number of molecules, where k/k_0 is the ratio of k , the molecular conductivity of the solution, to its limiting value k_0 when $n = 0$, for a binary electrolyte, the required value of the vapour-pressure ratio $(p' - p'')/p''$ should be $n''/(N - an'')$. The corresponding depression t is

* F. Guthrie, 'Phys. Soc. Proc.,' vol. 1, p. 53, 1874.

taken from the vapour-pressure curve $a = 0$ and plotted against n . The results for HCl so far as they go, up to a depression of 29° , agree very well with this hypothesis, taking $a = 5$. They are plotted in the small scale diagram (fig. 7B), and the values of n are doubled to make the initial slope agree with the curve $a = 0$. Thus the observed depression $t = 28^\circ.8$ corresponds with an actual strength $n/N = 8.39/100$, but is plotted against $2n = 16.78$. The curve would otherwise be too steep.

The observations of Roozeboom* for CaCl_2 , treated in a similar manner, allowing for the fact that it dissociates into three ions, agree very well with $a = 9$. To avoid confusion the curve is plotted against $10n$. Thus the observed depression $t = -20^\circ$, corresponding to $n/N = 4.37/100$, is plotted against 43.7 . The two highest points, at $t = 40^\circ$ and 55° , lie somewhat off the curve, but accurate observations here would be very difficult, and the ionisation is uncertain. At $t = -55^\circ$, $n = 6.92$, and $n'' = 9.80$, Van't Hoff's rule, indicated by the curve marked Ca Ions, would give a depression of only 10° . The present rule gives $t = -61^\circ$, which is more nearly of the right order of magnitude, and illustrates the great influence of the hydration factor a . CaCl_2 is known to form hydrates containing a large number of water molecules. The usual hydrate contains six molecules. It is quite likely that it would take to itself three others in solution. The osmotic pressure at -61° , according to the formula (10), would be about 600 atmospheres. Taking $(p' - p'')/p'' = n''/(N - an'')$ the osmotic pressure would be infinite when $n'' = 11.1$, or $an'' = 100$. The solution would avoid this difficulty by crystallising, or by a change in the value of a . It is probable that mixtures of molecular complexes corresponding to different values of a may occur in very strong solutions.

The observations (Mg), fig. 7A, on the depression of the freezing-point of solutions of MgCl_2 , given in Landolt's tables, do not extend beyond $t = -13^\circ.61$, but so far as they go they indicate a value $a = 12$ for the number of H_2O molecules in each complex. Owing to the steepness of the curve, the observed depressions are plotted against the values of n doubled.

The curve (K) for KCl, which is of quite a different character, agrees very well with the degree of ionisation deduced from the electric conductivity, on the hypothesis that each of the n'' molecules takes *one* molecule of water. The curve for NaCl would coincide very closely with that for KCl if each molecule of NaCl took *two* molecules of H_2O , but the observations for NaCl do not appear to extend beyond $n = 1.8$. In plotting these observations n is not doubled and the initial slope is 2.066 owing to the ionisation.

* 'Zeit. Phys. Chem.,' vol. 4, p. 42, 1889.

Rise of the Boiling-point.

17. The rise of the boiling-point affords a means of verifying the theory at a different temperature, but the method is more difficult of application, and the available observations less numerous than in the case of the depression of the freezing-point. Kahlenberg's data for cane-sugar, KCl and NaCl,* are

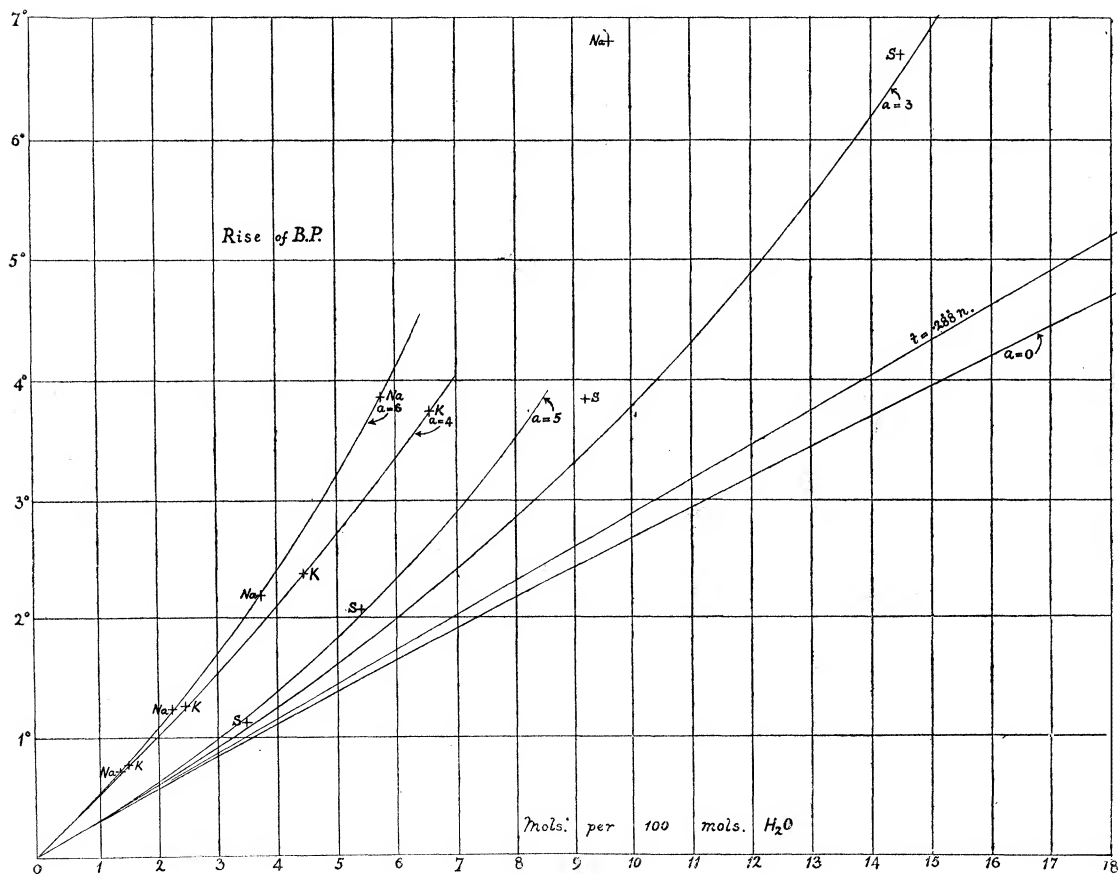


FIG. 8.—Rise of the Boiling-point in Aqueous Solutions.

plotted in the diagram, fig. 8. The curve $a = 0$ gives the relation between the vapour-pressure ratio $(p' - p'')/p''$ and the rise of temperature t above the boiling-point. The straight line $t = 0.288 n$ corresponds to Van't Hoff's ebullioscopic constant, the error of which is about 8 per cent. at $n = 10$. The observations (S) on the rise of the boiling-point for solutions of cane-

* L. Kahlenberg, 'Journ. Phys. Chem.,' vol. 5, p. 362, 1901.

sugar agree very fairly with the curve $a = 5$ up to a concentration of between 5 and 6 molecules of sugar to 100 of H_2O , which is about the limit of good agreement in fig. 5. It is perhaps remarkable that the number of H_2O molecules to one of sugar should apparently be the same at 100°C . as at 0°C . Beyond this point, as in fig. 5, the degree of hydration a appears to diminish, being about 4 on the average at $n = 9$, and 3 at $n = 15$. This is perhaps to be expected, as the mass of the sugar at $n = 15$ is about three times the mass of the water present, and the osmotic pressure, when the rise of the boiling-point is $6^\circ\cdot7$, is about 405 atmospheres.

No data appear to exist for the dissociation of electrolytes at or above 100°C . It is probable, however, that the dissociation does not change very greatly with temperature. The enormous increase in the conductivity of electrolytes with rise of temperature is to be explained chiefly by diminution of viscosity. Taking Kahlenberg's data for the dissociation of KCl and NaCl at 95°C ., the observations (K) on the elevation of the B.P. for solutions of KCl agree very well with the vapour-pressure theory, if $a = 4$, so far as the data for the dissociation extend, namely up to $n = 6\cdot5$. Beyond this point there is one observation at $n = 11\cdot82$, $t = 7\cdot60$, which appears to lie nearly on a continuation of the same curve. The observations for NaCl (Na) agree very well with the curve $a = 6$, up to $n = 6$. The highest point, at $n = 9\cdot63$, lies below the curve. The discrepancy may be due to errors of observation, or may indicate a systematic divergence. The agreement is much better than would be expected considering the difficulty of the observations, and the uncertainty of the dissociation data. It is noteworthy that both KCl and NaCl appear to annex many more molecules of H_2O at 100°C . than at 0°C . The dissociation data for the other electrolytes examined by Kahlenberg do not extend sufficiently far to be applicable.

Effect of the Heat of Dilution.

18. It is important to enquire how far the simple and convenient assumption made with regard to the dependence of vapour-pressure of a solution on its concentration is consistent with thermodynamical principles. The variation of the vapour-pressure of a solution with temperature is readily obtained by the circuit method in terms of the latent heat of vaporisation. What we require in the present case is the variation of the ratio p'/p'' of the vapour-pressures of solvent and solution. This is immediately given by a circuit similar to fig. 6 in which the branch AB representing ice is replaced by solution. Since the vapour-pressures of solution and solvent are not the same at θ_0 , we must insert an additional motor in the branch AC.

If double dashes, as usual, refer to the solution, and single dashes to the solvent, we thus obtain the equations,

$$(L''-L')-(L_0''-L_0') = \int_{\theta_0}^{\theta} (s'-s'') d\theta, \quad (29)$$

$$(L''-L')/\theta-(L_0-L_0')/\theta_0 = \int_{\theta_0}^{\theta} (s'-s'') d\theta/\theta + \int_{p''}^{p'} v dp/\theta - \int_{p_0''}^{p_0'} v dp/\theta_0. \quad (30)$$

Since $L''-L' = Q$ (§ 11), the heat evolved on dilution per unit mass of solvent added, the first equation gives the variation of the heat of dilution with temperature in terms of the difference of the specific heats of the pure solvent s' , and of the solvent in solution, which is represented by s'' . Writing $q = dQ/d\theta$ as an abbreviation for $s'-s''$, we obtain the required equation of vapour-pressure in terms of Q and q ,

$$(R/m)(\log_e(p'/p'')-\log_e(p_0'/p_0'')) = -Q_0t/\theta\theta_0 + \frac{1}{\theta} \int_{\theta_0}^{\theta} q d\theta - \int_{\theta_0}^{\theta} q d\theta/\theta, \quad (31)$$

where Q_0 is the latent heat of dilution at θ_0 .

We observe immediately that the ratio p'/p'' cannot be constant unless Q is zero. This is a well-known result, and is approximately true for solutions of many substances. For such substances it is perfectly justifiable to employ the vapour-pressure relation $(p'-p'')/p'' = n/(N-an)$, and it is highly probable that the hydration factor a will not vary greatly with temperature or with concentration, as we have seen to be the case with solutions of cane-sugar.

If Q is not zero, equation (31) gives a condition which must be satisfied by corresponding variations of a or n . In many solutions the number of effective molecules n'' varies continuously with temperature according to the degree of association or dissociation of the molecules of the solute. The factor a may also vary, but it appears in general to have a simple integral value which remains constant for considerable ranges of concentration and temperature, as we have seen in the case of electrolytes.

Equation (31), like the analogous equation for the ratio of the vapour-pressures of ice and water, may take a variety of forms according to the mode in which Q varies with temperature. If Q is constant, or $q = 0$, the equation reduces to a form similar to that commonly employed by physical chemists for deducing heats of solution from observations of solubility, or *vice versa*. The two cases are evidently very closely analogous, and the solubility equation may be deduced by the circuit method in a precisely similar way. Substituting for the vapour-pressure in terms of the osmotic pressure from equation (10), we obtain in this case for the variation of the osmotic pressure with temperature,

$$PU/\theta - P_0U_0/\theta_0 = -Q_0t/\theta\theta_0.$$

The osmotic pressure will not be proportional to the absolute temperature if $Q = 0$, unless U is also constant. But the proportionality may hold even if Q is not zero, provided that U varies in a suitable manner.

If q is not zero, we obtain solutions like (IV), (V), and (VI) for the vapour-pressures of ice and water, by making corresponding assumptions for q , and the form of the solution may vary widely from that usually assumed. Another case of special simplicity is that in which Q varies as θ , or $q = Q_0/\theta_0$, which gives

$$\log_e(p'/p'') - \log_e(p'_0/p''_0) = -(mq/R) \log_e(\theta/\theta_0),$$

in which case the ratio of the vapour-pressures varies inversely as $\theta^{mq/R}$.

We may further observe that if Q is constant, PU is a linear function of θ , though not proportional to θ , thus,

$$PU = P_0U_0 + (P_0U_0 - Q_0)t/\theta_0,$$

and that if $q = 2Q_0\theta/\theta_0^2$, as in equation (VI) for the vapour-pressures of ice and water, PU is a quadratic function of t , namely,

$$PU = P_0U_0 + (P_0U_0 - Q_0)t/\theta_0 - Q_0(t/\theta_0)^2.$$

It is useful to remember the physical meaning of the coefficients in these expressions, which might naturally be applied to represent the variation of the osmotic pressure with temperature. It also follows from the first expression that if Q is constant and equal to P_0U_0 , the product PU will be independent of the temperature, to the degree of approximation represented by equation (10).

Heat of Dilution and Ionisation of HCl.

19. As an example of the order of magnitude of the effects to be expected, we may take the case of solutions of HCl, for which the heat of dilution is one of the largest known. The quantities actually observed in a calorimetric experiment are the integral heats of solution and dilution obtained by making a solution of known composition and diluting with finite quantities of solvent, involving considerable changes in the concentration. The heat of dilution Q for an infinitesimal change, required in equation (31), may be deduced from the calorimetric observations as follows. By plotting the quantities of heat liberated when 1 gramme-molecule of solute is dissolved in X gramme-molecules of solvent (which is the way in which the observations are generally recorded) against the concentration C'' in grammes of solute per gramme of solvent, or against n/N for the resulting solution, we obtain the total heat of formation of the solution

Q'/n per gramme-molecule of solute as a function of the concentration C'' or n/N . In the case of HCl the curve is very nearly a straight line,*

$$Q'/n = 17,340 - 5920 C'' = 17,340 - 12,000 n/N. \quad (32)$$

The heat of solution at concentration n/N , or the heat evolved on adding a small quantity dn to a large mass of solution per gramme-molecule added, is represented by dQ'/dn , and is given by the equation,

$$Q'' = dQ'/dn = 17,340 - 24,000 n/N. \quad (33)$$

The heat of dilution at concentration n/N , or the heat evolved on adding a small quantity of solvent dN to a large mass of solution per gramme-molecule added, is represented by $Q = dQ'/dN$, and is given by the equation,

$$Q = dQ'/dN = +12,000 (n/N)^2. \quad (34)$$

If n molecules of solute are added to a large quantity of solution of concentration n/N , the heat evolved is nQ'' . If N molecules of solvent are added, the heat evolved is NQ . The sum of these two operations must be equal to the heat of formation Q' of a quantity of solution containing n molecules of solute to N of solvent. In other words, we have the relation $NQ + nQ'' = Q'$, which is evidently satisfied.

The heat of dilution Q , which is the quantity with which we are immediately concerned, is very large in the case of HCl, but is given by a very simple expression. In other cases, *e.g.*, H_2SO_4 , the curve is less simple, but may generally be represented as consisting of straight lines, which probably correspond to the formation of different hydrates or ions.

In the case of HCl, the depression of the freezing-point is approximately 40° for a solution for which $n = 10$ and $N = 100$. By equation (34) the heat evolved is 120 calories when 1 gramme-molecule of water is added to a large quantity of solution of this concentration. The heat evolved *per gramme* of water added, which is denoted by Q in equation (31) (deduced by taking *unit mass* of solvent round the circuit), is 6.67 calories. We see that, even in this very extreme case, the heat of dilution is a comparatively small fraction of the latent heat of fusion, namely, 79.5 calories, and will not greatly influence the curve of vapour-pressure. For dilute solutions, the effect will in any case be practically negligible, since it varies as the square of the concentration.

Since evolution of heat in any case is mainly connected with combination or dissociation of molecules, it is not at all unlikely that the heat of dilution may be accounted for in the majority of cases by the change in the

* The observations appear to have been smoothed to agree with Thomsen's hyperbolic formula, which inverts into the straight line above given.

effective number of molecules n'' in the vapour-pressure formula. This would account to a great extent for the surprisingly good agreement obtained in the case of electrolytes on the assumption $\alpha = \text{constant}$. It may be remarked that the agreement obtained in any case depends greatly on taking values of the ionisation as near the required temperature as possible. As might naturally be expected, the agreement of the observations at 100°C. is greatly impaired if values of the ionisation at 18°C. are taken. On the other hand, the agreement of the observations on the depression of the freezing-point is considerably improved, especially for dilute solutions, if values of the ionisation at 0°C. are employed in place of the values at 18°C. Values of the ionisation at 18°C. were at first employed in constructing the diagram, fig. 7, as being the more accurate, and more readily accessible. It did not appear to be worth while to redraw the curves employing the data for the ionisation at 0°C. when accessible, because the data were incomplete, and because the general conclusions remained unaltered. Although the agreement with theory was in many cases greatly improved, the uncertainty of the result for large values of the depression still remained.

The relation of the heat of dilution to the heat of ionisation and hydration is a most important and interesting question, but the data do not appear to be sufficiently complete, and it would be better to postpone the discussion of this point.

On the Hydrate Theory of Solution.

20. The theory of vapour-pressure and osmotic pressure outlined in this paper appears to afford the most direct method hitherto proposed of calculating the composition of definite molecular compounds, analogous to hydrates, occurring in solutions. The hypothesis apparently permits the extension, in a slightly modified form, to strong solutions of general principles which have hitherto been applicable only to dilute solutions. The existence of hydrates in solution has often been maintained, and has been supported by much indirect experimental evidence, but the theory has usually been stated in a manner which was open to serious objection. The essential point of a hydrate theory (as opposed to a diffusion-, or solution-pressure-, or gas-pressure-, or variable-aggregation theory) is the formation of definite hydrates according to the fundamental law of chemical combination. The difficulty of such a theory has been to determine the value of the hydration factor α , and to show that it was constant within certain limits, and equal to a simple integer. I have endeavoured to indicate how this may be determined, and I think I may fairly claim to have made out a good *prima facie* case for a modified form of the hydrate theory.

The problem has recently been attacked by H. C. Jones and his assistants at Johns Hopkins University, from a study of the depression of the freezing-points of strong solutions. They have accumulated a great deal of material, but I cannot agree with their interpretation of the results. Their experimental data appear to agree fairly in most cases with the vapour-pressure theory here given, but there are a few notable exceptions. The observed depressions of the freezing-point, for glycerol, $C_3H_5(OH)_3$, given by Jones and Getman* are from three to four times as large as those given by Abegg,† and cannot be fitted by any value of a . The data given by Jones and Bassett‡ for $CaCl_2$ differ considerably from those of Roozeboom,§ and do not agree at all well with the curve in fig. 7B.|| The authors have worked out their results on the assumption of a constant value for the theoretical molecular lowering of the freezing-point, and have obtained widely varying values of the degree of hydration, *e.g.*, from 140 molecules to 12 in the case of glycerine, and 30 to 13 for $CaCl_2$. Their final conclusions, which are diametrically opposed to the theory given in the present paper, are best stated in their own words:

Quotation from Jones and Bassett.¶

“*The Old and the New Hydrate Theory.*—The theory of hydrates in aqueous solutions that we believe to have established by the work, of which this is only a chapter, is to be sharply distinguished from the old hydrate theory of Mendeléeff, which, having long since been shown to be untenable, has been abandoned. According to the older theory, when a substance, like calcium chloride, is dissolved in water, there are formed certain definite chemical compounds, with perfectly definite amounts of water.

“According to the theory established by this work, the compounds formed are, at best, very unstable and vary in combination all the way from 1 molecule of water to a very great number. The composition of the hydrate formed by any given substance is purely a function of the concentration of the solution, or is determined, as we say, by the effect of mass action. Thus the composition of the hydrates formed by calcium chloride may vary all the way from a few molecules of water up to at least 30 molecules, and may have all intermediate compositions, depending solely upon the concentration, temperature being, of course, understood to be constant.

“It is thus obvious that the older and the newer hydrate theories are fundamentally different in character.”

Among recent evidence for the existence of hydrates in solution, the

* ‘*Amer. Chem. Journ.*,’ vol. 32, p. 320, 1904.

† ‘*Zeit. Phys. Chem.*,’ vol. 15, p. 217, 1894.

‡ ‘*Amer. Chem. Journ.*,’ vol. 33, p. 546, 1905.

§ ‘*Zeit. Phys. Chem.*,’ vol. 4, p. 42, 1889.

|| *Footnote added April 12, 1908.*—One of my students, Mr. W. F. Higgins, working under Mr. S. W. J. Smith’s direction, has verified the F. P. depressions in the case of glycerine and calcium chloride. His results agree with those of Abegg and Roozeboom respectively.

¶ ‘*Amer. Chem. Journ.*,’ vol. 33, p. 584, 1905.

experiments of Caldwell on the hydrolysis of sugar may be cited.* He attributes the accelerating influence of concentration to the hydration of the sugar molecules, though the degree of hydration cannot be calculated, because the rate of change may be affected by so many other factors. Similarly the degrees of hydration of various salts are estimated by observing the dilution required to reduce the constant K to its normal value. The values thus obtained appear somewhat high, because the possible effects of ionisation are expressly ignored. Whether ions are charged atoms, or whether they are merely unstable hydrates, it seems impossible to ignore their existence. Taking account of the ionisation factor, which is nearly 2 in a solution containing 1 grammie-molecule per litre, the water abstracted by the calcium chloride should be 18 grammie-molecules, according to the freezing-point depression, a result which does not differ greatly from Caldwell's estimate of 22 molecules. The residual difference in this and other cases may well be due to some accelerating influence of the ions as such, which could not be estimated satisfactorily unless allowance were made for the concentrating influence of hydration.

[*Note added March 17, 1908.*—Similar results for the degree of hydration have been deduced by J. C. Philip† from measurements of the solubility of oxygen and hydrogen in various solutions. The degree of hydration found for cane-sugar from Steiner's observations on the solubility of hydrogen was from 5.5 to 6.5 molecules of water to each molecule of sugar, which agrees as nearly as could be expected with the vapour-pressure theory. For salts, not allowing for ionisation, the values obtained for a are higher and more variable than those given by the vapour-pressure theory, *e.g.*, KCl 7 to 11, H_2SO_4 8 to 12, $CaCl_2$ average 21, etc. These values may indicate a specific effect of the solute, apart from mere hydration. Oxygen seems to give different results from hydrogen, *e.g.*, NaCl average $a = 11$ from hydrogen, $a = 14.7$ from oxygen. The method does not appear to succeed so well with more soluble gases or other indifferent substances. It is less simple and direct than the vapour-pressure method, and the effect observed is likely to be more complex.

A large number of data exist for the relative lowering $(p' - p'')/p'$ derived from direct measurements of the vapour-pressure, especially in the case of salt solutions. Very few of these are available for deducing the degree of hydration, either because the ionisation data are deficient, or because the direct measurements of small vapour-pressures are necessarily somewhat

* 'Roy. Soc. Proc.,' A, vol. 78, p. 272.

† 'Faraday Soc. Trans.,' vol. 3, p. 140, 1907.

inexact. But, so far as they go, they appear to be in fair agreement with the vapour-pressure theory.]

General Summary of Conclusions.

21. The foundation of the vapour-pressure theory of solutions here laid down is the assumption of a simple relation between the vapour-pressure and the molecular constitution of the solution. That there should be a simple relation of this kind appears extremely probable when we consider that the concentration of the vapour phase in the solutions here examined is very small, and that such relations generally take a very simple form at extreme dilution. That such a relation should serve as a key to many of the phenomena occurring in solutions is not surprising in view of the fact that equality of vapour-pressure is one of the most general conditions of equilibrium in physical chemistry. The relation of this assumption to the gas-pressure theory, or the hydrate theory, or the capillary-pressure theory, as already indicated, is that it involves them all, since they may be regarded as merely different aspects of the same phenomena. An equivalent assumption may be formulated, at least approximately, in terms of partial pressure, or capillary pressure, or chemical attraction, but it would merely be putting the same thing in different words. The vapour-pressure method appears to be the most direct line of attacking the problem. If, for instance, we regard the changes of capillary pressure in relation to vapour-pressure as defined by the relation $U dP = v dp$, we should arrive at nearly the same result by similar approximations. But this method does not appear to be so convenient, because it involves the volume U , which is generally unknown and variable in an uncertain manner, whereas the volume of the vapour v at low pressures may be regarded as conforming very closely with the laws of gases.

There is no doubt that further experimental work may be required to establish the vapour-pressure theory generally, since accurate data for strong solutions are comparatively scarce. The interpretation of the ionisation factor, and its relation to the heat of dilution, requires further elucidation. Analysis of nearly all the data at present available, in addition to the examples above cited, fails to show any serious disagreement with the vapour-pressure theory. The theory cannot pretend to be exact for all ranges of temperature and concentration, but it seems likely to serve, at least as a second approximation, for co-ordinating results which have hitherto appeared discordant.
